

***TERNARY NUCLEATION MECHANISMS AND NEW
PARTICLE FORMATION***

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*For Presentation at
Second Workshop on Formation and
Growth of Atmospheric Aerosols,
Monticello MN
September 8-9, 2006*

September 2006

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Ternary Nucleation Mechanisms and New Particle Formation

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INTRODUCTION

Recent kinetic extensions of the nucleation theorem (KNT) suggest that the logarithm of the steady-state nucleation rate has strong multi-linear dependence on the log concentrations of condensable species present in the vapor phase. A further remarkable result is that the coefficients of this linear dependency provide a direct determination of the molecular content of the critical nucleus itself.

The new approach is applied to recent measurements by Zhang and co-workers on the p-toluic acid/ sulfuric acid/water ternary vapor system. A linear minimum variance parameterization for nucleation rate dependence on vapor composition, accurate over the range of the measurements, is obtained. Estimates of critical nucleus composition are also presented. These show that a single molecule of p-toluic acid present in the critical nucleus is sufficient to trigger a ternary nucleation event.

Current research is focused on the mechanisms and rates by which critical nuclei (particles of about 1nm in size), once formed, reach climate-significant size.

TERNARY NUCLEATION MECHANISM

The work described here was carried out in collaboration with Renyi Zhang at Texas A&M (Zhang et al., 2006; McGraw and Zhang, 2006). Analysis here will focus on the ternary system p-toluic acid/sulfuric acid/water to illustrate the new methods, which enable characterization of the critical nucleus and parameterization of the nucleation rate for use in models.

There is a strong propensity, at least locally on the nucleation rate surface, for the nucleation rate to be a multilinear function of vapor species concentrations and temperature when all variables are cased in appropriate form. From the kinetic nucleation theorem (McGraw and Wu, 2003), we find:

$$\ln J \approx \ln J_0 + \sum_i (g_i^* + \delta_i)(\ln n_i - \ln n_i^0) - \frac{\Delta E(g_1^*, g_2^*, \dots)}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (1)$$

where J is the nucleation rate, n_i is the vapor phase concentration of species i , g_i^* is the number of molecules of species i in the critical nucleus, δ_i is a small kinetic factor (between 0 and 1), ΔE is the energy required to form the critical nucleus (having the specified composition) from the vapor, k is the Boltzmann constant and T is temperature. According to Eq. 1, a multilinear analysis of nucleation rate measured as a function of vapor composition and temperature can provide a direct determine of critical nucleus properties – molecular content and cluster energy. The Zhang et al. measurements are at constant temperature, so only the first terms in Eq. 1 are significant and the cluster energy cannot be determined. Furthermore the measurements are at constant relative humidity, and so the water content of the critical nucleus cannot be determined. This leaves the three variables: J , and vapor phase concentrations of organic and sulfuric acids.

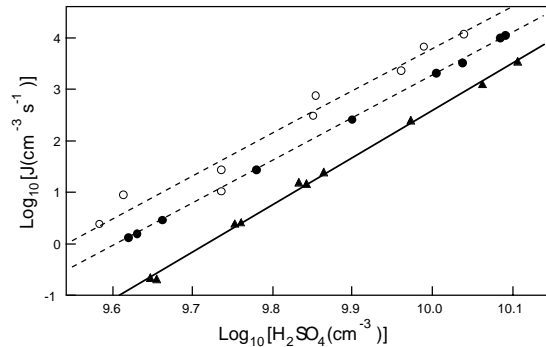


Figure 1. Measurements from Zhang et al. (2004) for the ternary system system p- toluic acid/sulfuric acid/water plotted in nucleation theorem motivated coordinates, log nucleation rate (J) versus log sulfuric acid vapor concentration. Filled circles, p-toluic acid concentration = 0.2ppb. Open circles, p-toluic acid concentration = 0.4ppb. Triangles, binary sulfuric acid-water measurements. Solid line, least-squares fit to the binary data. Dashed lines, projections from the linear minimum variance estimator (LMVE) plane (Eq. 2) evaluated at the two p-toluic acid concentrations (these parallel lines live on the same plane and when projected, as shown here, have the same slope).

The figure shows conformity to Eq. 1 for these remaining three variables. Under ternary conditions, the measurements are expected to lie on a 2D plane in the 3D coordinate space, and it is clear from Fig. 1 that they do ($R^2 = 0.98$). The planar fit takes the simple form:

$$z = -76.75 + 8.12x + 1.86y \quad (2)$$

where $z = \text{Log}_{10}[J_T, \text{cm}^{-3}\text{s}^{-1}]$,
 $x = \text{Log}_{10}[H_2SO_4, \text{molecules cm}^{-3}]$, and
 $y = \text{Log}_{10}[\text{Organic}, \text{ppb}]$ for the ternary nucleation rate. Comparison of Eqs. 1 and 2 immediately yields a critical nucleus composition of 8 molecules of sulfuric acid and just a single molecule of the organic acid. Other ternary systems that we have examined of this type – having only different organic acids – show a similar trend. Namely, just a single molecule of the organic acid is present in the critical nucleus, along with a similar number (about 8) molecules of sulfuric acid. Measurements on the benzoic acid system at two different values of the RH furnish a crude estimate of the water content – we estimate about 17 molecules of water present in the critical nucleus, but there is large uncertainty to this last value.

NEW PARTICLE FORMATION

Figure 1 presents a bit of a paradox when compared with atmospheric measurements of new particle formation. Specifically the relative rate sensitivities $\partial \text{Log}_{10} J / \partial \text{Log}_{10}[H_2SO_4]$ as measured in the lab are much higher than in the field. Thus we observe a slopes of 9 and 8 for the binary and ternary rates,

respectively, compared with observations at Mauna Loa, HI, and Idaho Hill, CO, which found values only between 1 and 2 [Eisele and McMurry, 1997]. We are currently investigating this discrepancy and will report preliminary results along with a method of moments analysis of the mechanisms and rates by which critical nuclei (particles of about 1nm in size), once formed, reach climate-significant size.

Keywords: Nucleation, new particle formation, kinetic nucleation theorem

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This work was supported by the U. S. Department of Energy Atmospheric Sciences Program under Contract NO. DE-AC02-98CH1-886